



Facile synthesis of PdO-doped Co₃O₄ nanoparticles as an efficient bifunctional oxygen electrocatalyst

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ABSTRACT

The interfaces of multicomponent hybrid nanoparticles (MHNPs) have great effects on their electrocatalytic activities. Herein, a highly active multifunctional catalyst heterostructure PdO-doped Co₃O₄ (PdCo-300) nanoparticles with closely mutually connected interfaces were synthesized by a convenient strategy. The prepared PdCo-300 nanoparticles displayed high catalytic activities for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline media. The results show that the considerable electrocatalytic activities and stabilities are associated with the formation of MHNPs with intimate connected boundary between PdO and Co₃O₄. At the interface, the decrease of Pd electron density (downshift of the d-band center) and the formation of large amount of oxygen vacancies in Co₃O₄ promoted the electrocatalytic performance. Theoretical calculations show that the synergy of Pd ions and Co ions at the interface can enhance the interaction between active oxygen species and the catalyst surface, resulting in the decrease of energy barrier for ORR.

1. Introduction

With the increase of the energy crisis and rising concerns of environmental issues, the world more urgently needs the advanced clean energy conversion technologies than ever before [1,2]. Metal–air batteries and polymer electrolyte membrane fuel cells (PEMFCs) have been proven to be the promising candidates as the class of energy conversion devices to provide clean and sustainable power, and oxygen electrocatalysis plays a critical role in the next-generation devices [3–5]. Moreover, the promising clean energy technologies of rechargeable metal–air batteries and regenerative fuel cells require the electrocatalysts with high voltage outputs and low over-potentials for ORR and OER [6,7]. Generally, the electrocatalysts (such as Pt-based materials) are favorable for ORR usually tends to be poor for OER and vice versa [8–10]. Therefore, it is a great challenge to develop the multifunctional electrocatalytic materials to drive both ORR and OER with high activity and low cost for the practical applications of clean energy technologies.

Among various metal elements, Pd has been considered as a promising candidate to replace Pt-based electrocatalysts for their similar crystal structure and lattice constant [11–13]. Great efforts have been made on modification of the electronic structure of Pd to enhance the catalytic activity by controlling their morphologies [14–16], alloying

Pd with foreign metals [17–20], or supporting Pd on metallic oxide [21–23]. Libuda et al. reported that for the catalyst of Pd supporting on Fe₃O₄, a thin PdO_x layer at the particle/support interface can be formed when initial oxidation of the metal atoms. This strong interaction can modify the electronic structure of Pd and enhance the catalytic activity [24]. Recently, Co₃O₄ as one of the most popular spinel type metal oxide, are the great investigated in the literature due to their rich redox chemistry, high electrocatalytic activity and lower cost [25–29]. Meanwhile, the cobalt ions existing in mixed valences make them easily act as donor-acceptor chemisorption sites for the reversible adsorption of oxygen in the electrooxidation reaction [30]. It is well-known that MHNPs joined together through metal-oxide interfaces can facilitate synergistic interaction and show preferable catalytic activity and stability [31]. Drawing inspiration from outstanding electrocatalytic activity of Co₃O₄ and Pd, PdO-doped Co₃O₄ nanoparticles with well-defined structure might ensure an excellent electrocatalytic activity.

Herein, a highly active multifunctional catalyst heterostructure PdO-doped Co₃O₄ nanoparticles with closely mutually connected interfaces were synthesized by air-oxidation treatment the PdCo nanoparticles. The PdCo nanoparticles were obtained according to our previous work [32]. The activity and durability toward ORR and OER of the PdO-doped Co₃O₄ nanoparticles were evaluated, and the

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mechanisms behind its excellent performance were elucidated.

2. Experimental

2.1. Synthesis of the catalysts

Briefly, 1.65 mmol EDTA (0.1 M) aqueous solution was mixed with 0.2 mmol H_2PdCl_4 (0.05 M) solution and 1.45 mmol $\text{Co}(\text{NO}_3)_2$ (0.1 M) solution. Then the resulting mixture solution was quickly injected into 8.2 mmol NaBH_4 (0.1 M) aqueous solution with vigorous stirring in an ice water bath. The resultant black powder was collected by centrifugation, washed with deionized water three times, and dried overnight at 70 °C. The precursor was formed and denoted as PdCo. The catalyst was prepared by annealing the precursor powder at 300 °C for 2 h in air at a heating rate of 2 °C/min and denoted as PdCo-300. Pd-300 and Co-300 were also synthesized via similar procedure. The precursor PdCo annealed at different temperatures (200 °C, 400 °C and 500 °C) for 2 h were also carried out and denoted as PdCo-200, PdCo-400 and PdCo-500, respectively.

2.2. Characterization

X-ray powder diffraction (XRD) measurements were performed using an X-ray diffractometer (Ultima IV-185, Rigaku) with filtered Cu K α radiation. The morphology of the samples was measured by JEM-2100 transmission electron microscope (TEM). The X-ray photoelectron spectroscopy (XPS) was recorded by VG ESCALAB 210 instrument equipped with Mg K α radiation. The whole electrochemical experiments were measured with a CHI 660E electrochemical workstation (Chenhua Instruments Corp, Shanghai, China).

2.3. Electrochemical measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were measured with a rotating disk electrode (RDE) controller (AFMSRCE, Pine Instrument Co.) connected to a CHI 660E electrochemical workstation. A three-electrode system was applied, with Hg/HgO electrode and Pt wire as reference electrode and counter electrode, respectively. The catalyst film-coated glassy carbon working electrode are prepared as follow: (i) 3 mg of the electrocatalyst and 7 mg of Vulcan XC-72 were dispersed into 1 mL ethanol containing 50 μL 5 wt.% Nafion solution by sonication for 30 min to form a homogeneous ink. (ii) 6 μL of the ink was coated on the surface of glassy carbon electrode (GCE, 4 mm in diameter), resulting in a catalyst loading of 0.455 mg cm^{-2} . Commercial 20 wt.% Pt/C (Johnson Matthey) was used for comparison with the same powder loading.

3. Results and discussion

3.1. Structural and composition analysis

The morphologies of the prepared samples were characterized by transmission electron microscopy (TEM). PdCo (Figure S1) is present in a structure of mutually connected and fused irregular nanoparticles with clear edges. After the calcination treatments, the PdCo-300 (Figs. 1(a) and S2) nanoparticles exhibits more obscure boundaries. The irregular particles (darker contrast) can be seen surrounded by cloudy domain nanostructures (lighter contrast). The structure is expected to be the PdO domain surrounded by the Co_3O_4 domain, where the different contrasts in the transmitted electron intensities are due to their different mass to charge ratios [33]. Meanwhile, the high-resolution transmission electron microscopy (HRTEM) image further confirmed that the PdO domain was nested in the Co_3O_4 domain. As shown in Fig. 1(b–d), The darker, smaller nanoparticles were identified as PdO on the basis of a distinct PdO (101) lattice fringe with a spacing of 0.265 nm. At around Pd nanoparticles, the lattice fringe with an

interplanar spacing of 0.243 nm is ascribed to the (311) plane of Co_3O_4 , and the lattice spacing of 0.286 nm conforms to the (220) plane of spinel Co_3O_4 . At the boundary of PdO domains, some of Co_3O_4 seems to be amorphous because there was no clear lattice fringe observed in the HR-TEM image (Fig. 1(b–d)). The numerous amorphous regions imply that the PdCo-300 has a very poor crystallinity, which further confirmed by our following XRD analysis result [34]. The particles were found to be lattice-to-lattice coupled (Fig. 1(d),(e)), although the heteroparticles had different d_{spacing} orientations. Furthermore, a strained and defect-rich interface (Fig. 1(f)) was observed at the PdO and Co_3O_4 adjacent domain. These defects could tune the corresponding electronic redistribution for electrocatalysis and improve their electrocatalytic performance [35]. Fig. 1(g) shows a representative HADDF-STEM image of PdCo-300. The energy dispersive X-ray spectrometry (EDS) mapping analysis in Fig. 1(h–j) show that the elements Co, O and Pd are all presented in the PdCo-300. As shown in Fig. 1(i), Pd is homogeneously distributed in the bright region NPs in the HAADF image (Fig. 1(h)). In contrast, Co is mostly distributed in the boundary of Pd areas although its presence is strongly noted inside the Pd areas. These results demonstrate that Co_3O_4 nanoparticles are doped with PdO and the sample is presented in a structure with PdO surrounded by the Co_3O_4 domain.

XRD spectra of samples are shown in Fig. 2(a). For Pd-300, the peaks located at 33.8°, 41.9°, 54.7°, 60.2° and 71.5° are attributed to the (101), (110), (112), (103) and (211) planes of PdO (PDF# 41-1107). For Co-300, the two weak and broad peaks at about 36.9° and 65.4° are corresponded to the (311) and (440) facets of Co_3O_4 (PDF# 74-1657). As for the precursor of PdCo, the three broad peaks at 40.1°, 46.7° and 68.1° are attributed to metal Pd (111), (200) and (220), respectively (PDF# 46-1043). After calcination, the precursor of PdCo is transformed to PdCo-300, the peaks of PdO and Co_3O_4 can be observed for the PdCo-300. There was no diffraction peak of component Co observed in the precursor of PdCo, while two weak and broad peaks of Co_3O_4 can be observed in the PdCo-300, indicating the component Co do exists in the as-synthesized catalysts and are reduced in size with a poorly polycrystalline structure [34,36]. To further increase the annealing temperature, the Co_3O_4 XRD peaks intensity of PdCo-400 and PdCo-500 (Figure S3) became stronger and sharper, indicating that the higher temperature leads to better crystalline degree of final products [37]. It is worth noting that there was no diffraction peak of PdO observed in the PdCo-200 (Figure S3), while the peaks of Co_3O_4 can be observed, confirming Co is more easily oxidized than Pd. Meanwhile, compared to Pd-300, the peaks of metal Pd disappeared with the addition of Co in the PdCo-300, which may be attributed to the introduction of cobalt species can promotes the oxidation of palladium. The oxidation states and surface composition of the prepared samples were characterized by XPS. As presented in Fig. 2(b), two main peaks can be seen at about 780.0 and 795.2 eV, corresponding to the Co 2p $_{1/2}$ and Co 2p $_{3/2}$ spin-orbit peaks of Co_3O_4 [38]. In addition, two peaks exhibited at about 787.1 and 803.7 eV correspond to the shake-up satellite peaks of Co_3O_4 [39]. Importantly, the binding energy of Co 2p $_{3/2}$ and Co 2p $_{1/2}$ shifts to a higher value by 0.9 eV and 1.4 eV and the satellites are strengthen in PdCo-300, indicating more Co^{2+} component present in PdCo-300 [40]. The main peak can be fitted by two regions of Co^{2+} and Co^{3+} , and the $\text{Co}^{2+}/\text{Co}^{3+}$ ratios of PdCo-300 (1.5) is higher than that of Co-300 (1.1), indicating that a partial Co^{3+} ions are turn into Co^{2+} with the presence of Pd species during heat-treating process. According to the electro-neutrality principle, an increase in the Co^{2+} content means a rise in the amount of oxygen vacancies [41], that is, surface oxygen vacancies are more easily formed on the surface of PdCo-300 nanoparticles, which can be further confirmed by high-resolution O 1s XPS spectra. As shown in Fig. 2(c), the peaks at 529.8, 531.1, 532 and 533.8 eV can be ascribed to lattice oxygen (O^{2-}), peroxide (O^-), superoxide (O_2^-) and hydroxyl (OH^-), respectively [31]. Compared with Co-300, the major peak of Co 2p and O 1s of PdCo-300 shifting in the direction of high binding energy, which can be attributed to the different combination manner of

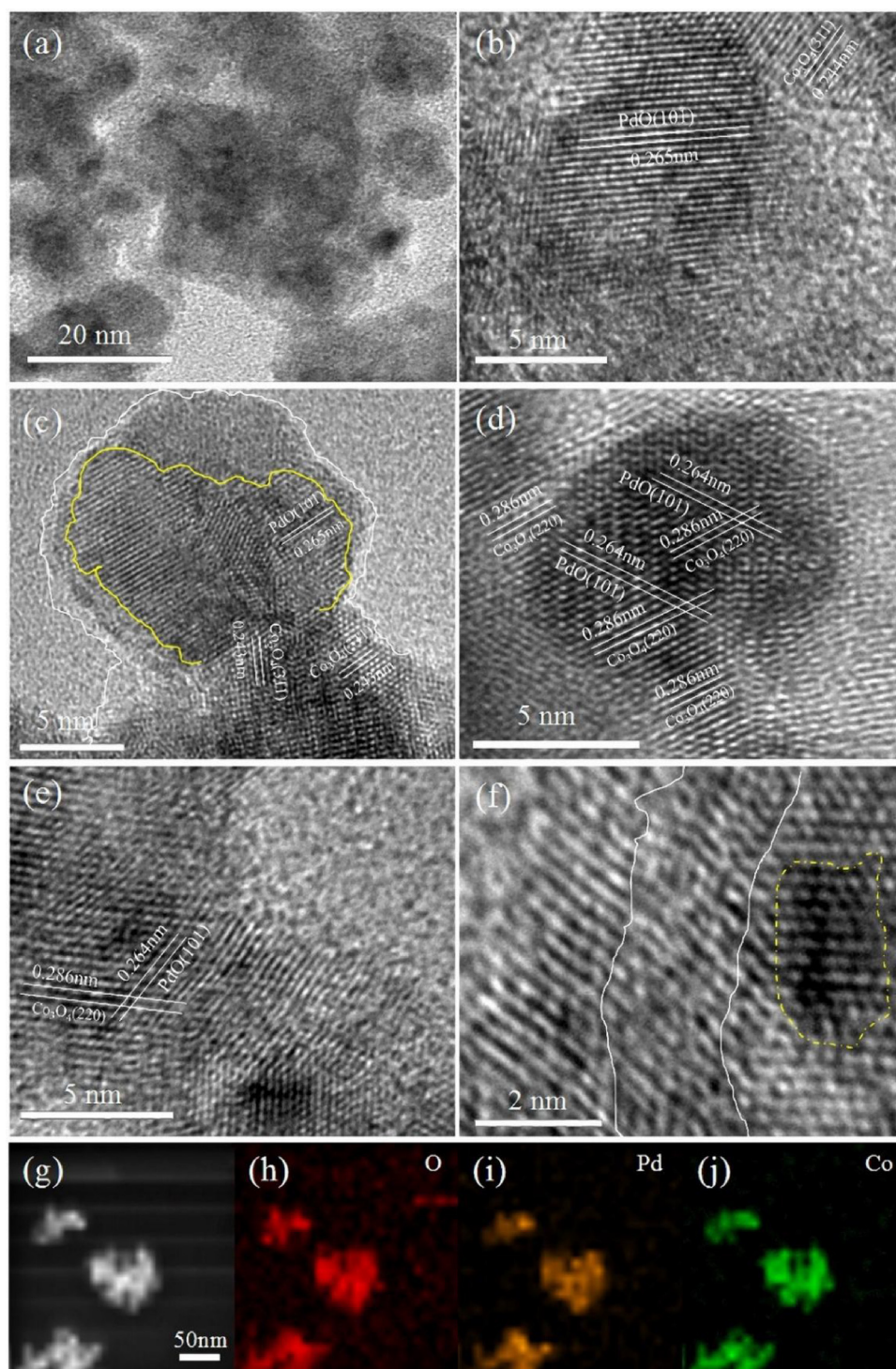


Fig. 1. Typical TEM images PdCo-300 (a), HR-TEM of PdCo-300 (b–d). EDX results for PdCo-300 sample along with: (g) HAADF image, and elemental mappings for (h) O, (i) Pd and (j) Co, respectively.

O^{2-} bonded with Co^{3+} and Co^{2+} on the surface of PdCo-300 nanoparticles [42]. Besides, the peaks of O^- and O_2^- species of PdCo-300 nanoparticles are obviously strengthened, which can be ascribed to more easily formed oxygen vacancies in PdCo-300. According to early studies, oxygen vacancies not only can activate adsorb oxygen and provide the lattice sites of oxygen migration, resulting in the formation of highly active electrophilic oxygen species, but also can generate new defective states in the energy band gap of Co_3O_4 and two electrons on the defective states are easily excited, leading to enhancement of the electronic conductivity of Co_3O_4 [43,44]. Fig. 2(d) shows the Pd 3d XPS

spectra of the Pd-300 and PdCo-300, the peaks at 335.5 and 340.8 eV are ascribed to Pd^0 , the peaks of at 337.2 and 342.6 eV are attributed to Pd^{2+} , the peaks at 337.6 and 342.6 eV are considered Pd^{4+} , and the peaks at higher bonding energy (339.7 and 345.3 eV) are considered to Pd-O junction or PdO_x [45,46]. It is noted that the metal Pd still presents in the Pd-300 even though annealing in the air for 2 h, while no peaks of metal Pd can be observed in the PdCo-300, which is further confirmed that the cobalt can promote the oxidation of palladium. Compared to Pd-300, the binding energy of Pd 3d for PdCo-300 shifted more positively. The positive shift could result in a decrease of the d -

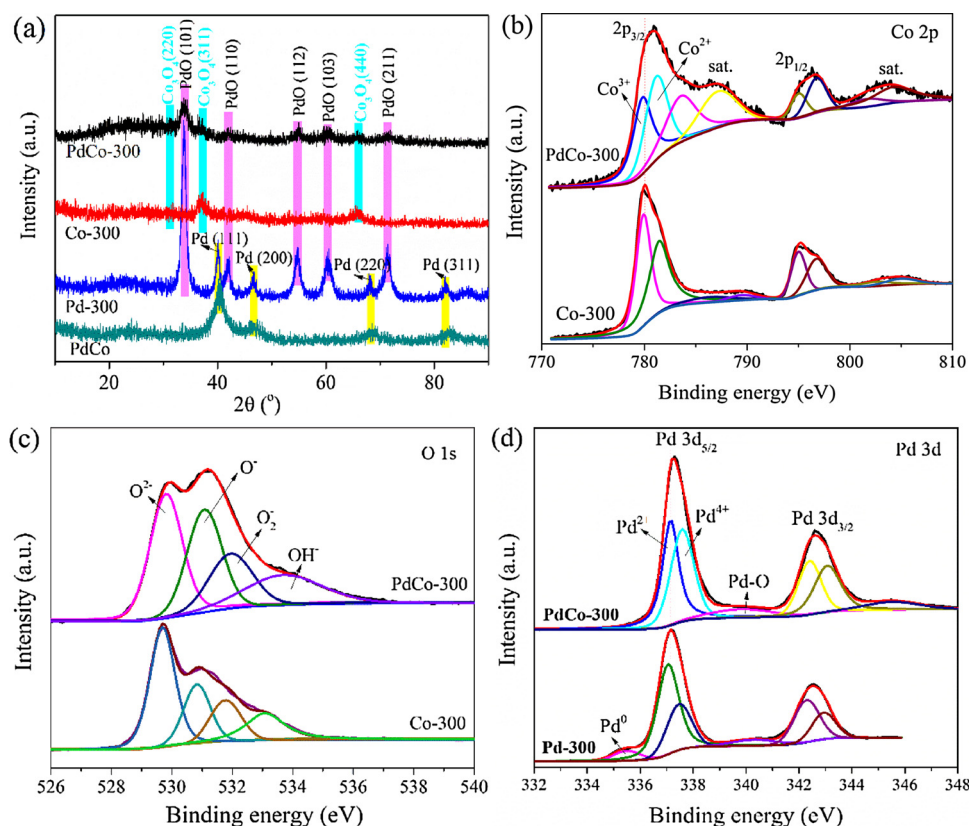


Fig. 2. X-ray diffraction (XRD) spectrum of PdCo, Co-300, Pd-300 and PdCo-300 (a), High-resolution XPS spectra of Pd-300, Co-300 and PdCo-300: Co 2p (b), O 1s (c) and Pd 3d (d), respectively.

band center in Pd, leading to a decrease of the surface coverage by the generated OH, and releasing more active sites on the Pd surface for O₂ adsorption, and thus enhancing the electrocatalytic activity [47].

Based on the XRD, TEM, and XPS analysis, we can give a reasonable description about the structure of PdCo-300. During the air-oxidation treatment of PdCo, Co is first converted to CoO. In this process, the diffusion of oxygen atoms is faster than cobalt atoms. Then, CoO is further oxidized to form Co₃O₄. The transition from CoO to Co₃O₄ is different from that of Co to CoO, the Co diffusion is more rapid than the O diffusion, resulting in Pd species being nested in the cobalt oxide phase after the oxidation treatment [48]. The formation of this structure is considered to be the Kirkendall-based mechanism [49]. Pd is transformed to PdO along with the rise of oxidation temperature and the prolongation of oxidation time. At the interface, a few Co ions enter the lattice of the PdO, which contributes to the higher Co²⁺/Co³⁺ ratios in PdCo-300. The exchange of Co and Pd species at the interface can be described as a reaction of Pd²⁺ + Co³⁺ → Pd³⁺ + Co²⁺ during the heat-treating process [42,50]. The oxide film can be grown either at the metal-oxide interface (in which case the transport of oxygen ions inside the nanoparticles prevails) or at the gas-solid interface (and then the transport of metal to the surface is dominating) [51]. In the case of a difference in diffusion coefficients, accumulation of vacancies at the metal oxide interface can lead to the formation of MHNPs with intimate connected boundary domains. Apparently, these closely mutually connected interfaces will result in the surface reconstruction around the interface, lattice mismatch and electron interaction/transfer across the interface, and lead to produce more catalytic active sites.

Based on the DFT calculation, we investigated the oxidation state of the Pd atom (see SI for detailed description about our DFT calculations). The calculated Bader charge of Pd atom in the PdO (P42/mmc) and PdO₂ (P42/mnm) crystal are 0.96e and 1.62e respectively (Figure S7). The charge of a Pd atom at the 4-fold coordination site in the Co₃O₄ cell (F-43 m) is 1.12e, while that of a Pd occupies a 6-fold coordination site

achieves 1.69e (Figure S8), which is larger than that of Pd⁴⁺ ion in PdO₂. In the poorly polycrystalline structure Co₃O₄, with the more complex coordination, Pd atom maybe achieve higher oxidation state [45].

3.2. Electrochemical testing

The samples with different annealing temperature for ORR and OER were shown in Figure S5 and Figure S6, respectively. We can see that the PdCo-300 displays the best catalytic activities than those of PdCo-200, PdCo-400 and PdCo-500. Therefore, we choose 300 °C as PdCo annealing temperature. The electrocatalytic performances of PdCo-300 and commercial Pt/C were first investigated by CV technique. As shown in Figure S4, there is an obvious reduction peak at about 0.7–0.8 V for all samples in O₂-saturated environment but no peak appears in N₂-saturated solution, suggesting all samples have catalytic activity for ORR. The ORR peak potential for PdCo-300 is about 0.81 V, which is more positive than those of Pd-300 (0.78 V), Co-300 (0.71 V) and PdCo (0.77 V), indicating PdCo-300 has better ORR catalytic performance. To further compare the ORR activity, the LSV tests were carried out with a sweep rate of 10 mVs⁻¹ at a rotation rate of 1600 rpm by RDE in O₂-saturated 0.1 M KOH solution. For comparison, the commercial Pt/C, Pd-300, Co-300 and PdCo were also tested at the same condition. As is shown in Fig. 3(a), the PdCo-300 displays the better ORR activity with the current density of -5.07 mA cm⁻² and the half-wave potential of 0.83 V, which is very close to those of commercial Pt/C (-5.1 mA cm⁻², 0.85 V), and higher than those of Pd-300, Co-300 and PdCo catalysts. Noticeably, Co-300 and Pd-300 display relatively lower ORR activity compared to PdCo-300, suggesting a synergistic effect between PdO and Co₃O₄. The polarization curves for ORR of PdCo-300 at rotation rates varying from 400 rpm to 1600 rpm are shown in Fig. 3(b), and the Fig. 3(c) shows the Koutecky-Levich plots. These plots were linear, indicating the first-order kinetics with respect to oxygen. The average

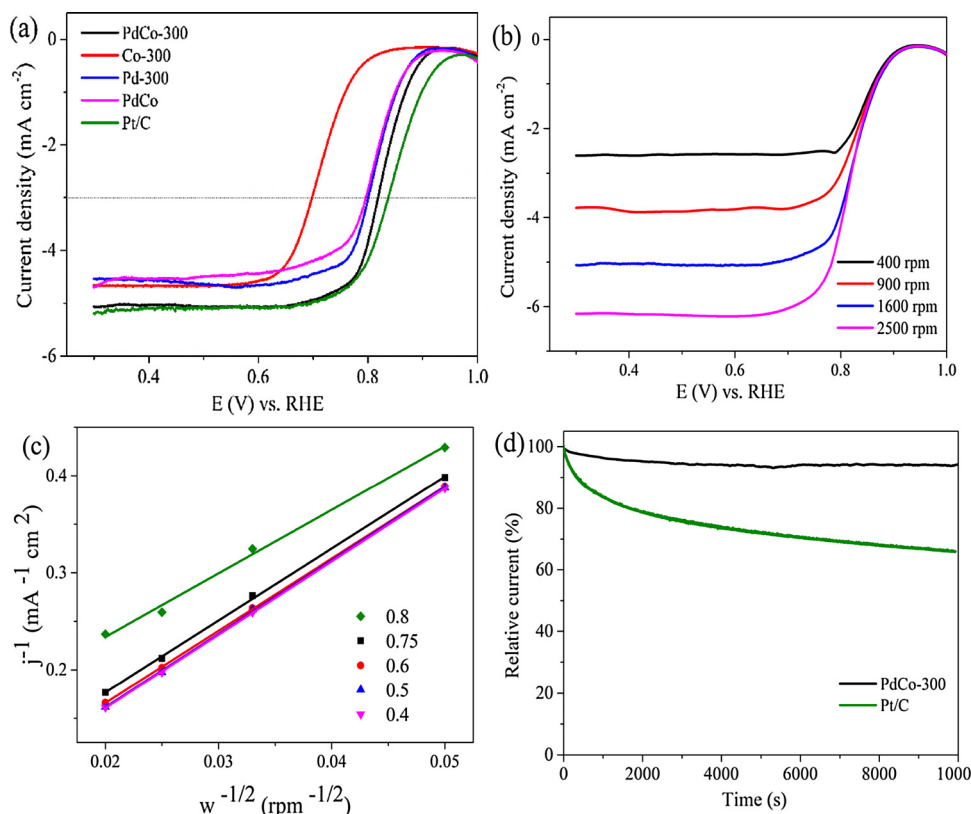


Fig. 3. LSV curves of the PdCo, Pd-300, Co-300, PdCo-300 and commercial Pt/C electrocatalysts on RDE electrode in O₂-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm with a scan rate of 10 mV s⁻¹ (a), LSV curves of PdCo-300 in O₂-saturated 0.1 M KOH solution at various rotation rates with a scan rate of 10 mV s⁻¹ (b), the corresponding Koutecky-Levich plots of PdCo-300 at different potentials (c), i-t chronoamperometric responses of PdCo-300 and commercial Pt/C at 0.75 V vs. RHE in O₂-saturated 0.1 M KOH (d).

transfer electron number was calculated to be 3.85 from 0.4 to 0.8 V (vs. RHE), suggesting a four-electron reaction for PdCo-300. Additionally, the PdCo-300 electrocatalyst exhibited an excellent stability with only 6% decrease in current after the test for 10,000 s (Fig. 3(d)), which is significantly superior to that of the commercial Pt/C (34% current decrease after the test for 10,000 s).

The catalytic activity of as-synthesized samples for OER were also investigated (Fig. 4(a)). It can be seen that PdCo-300 has a more negative OER onset potential than those of other samples. The potential required to oxidize water at the current density of 10 mA cm⁻² is a metric related to solar fuel synthesis [52]. Compared to Co-300, Pd-300 and PdCo, PdCo-300 shows a highest electrocatalytic activity for the OER with a potential of 1.58 V at a current density of 10 mA cm⁻², 60 mV negative than that of commercial RuO₂ (1.64 V). The multifunctional electrocatalytic activity was usually evaluated by the variance metrics ΔE ($E_{j=10 \text{ mA cm}^{-2}} - E_{j=-3 \text{ mA cm}^{-2}}$). A smaller ΔE

indicates the better electrocatalytic activity and more promising for practical use in fuel cells. As shown in Table S1, the PdCo-300 exhibited a superior bifunctional electrocatalytic activity with a smaller ΔE of 0.76 V than that of Pt/C (0.96 V) and most of the reported bifunctional electrocatalysts. Further durability measurements with a chronoamperometer for 10,000 s are presented in Fig. 4(b). After 10,000 s of continuous OER at 1.60 V, PdCo-300 showed 20% attenuation relative to its initial current density, whereas for the commercial RuO₂ and Pt/C, the attenuation was almost 38% and 50%, respectively.

3.3. Origin of the superior electrocatalytic activity of PdCo-300

We take ORR as example to elucidate the effect of the coexisted Pd and Co ions in the interface of PdCo-300 based on the DFT calculations. Some investigators justified that DFT calculated barriers can be used to estimate the redox barrier [53,54]. Both XRD and TEM indicated that

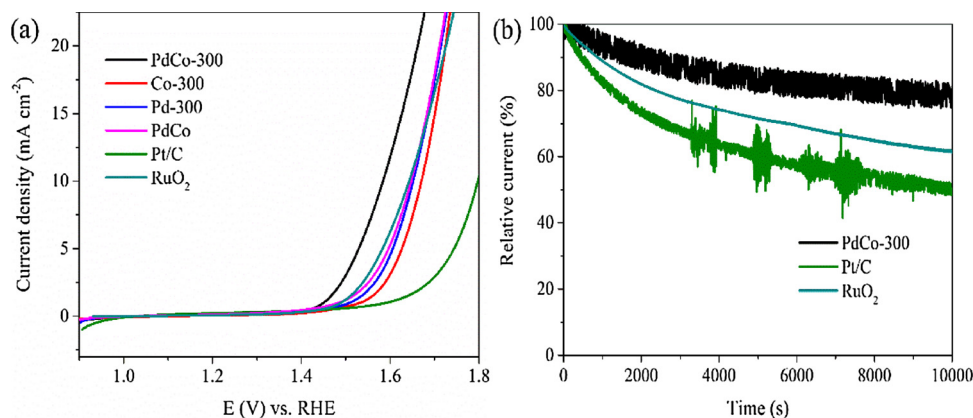
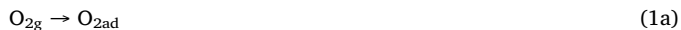
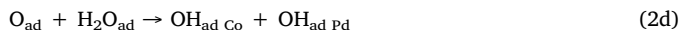


Fig. 4. LSV curves at 1600 rpm for PdCo, Pd-300, Co-300, PdCo-300, commercial RuO₂ and Pt/C in O₂-saturated 0.1 M KOH (a), i-t chronoamperometric responses of PdCo-300, commercial RuO₂ and Pt/C at 1.60 V vs. RHE in O₂-saturated 0.1 M KOH (b).

the PdO(101) surface was the main exposed surfaces. So, various of ORR mechanisms [55] on the pure PdO(101) surface were explored with DFT calculations in our work. The detailed calculation model and method were described in the SI. Our calculations showed that the favorable mechanism for ORR on the PdO(101) surface involves five elementary steps as follows:



The transition state structure and the Gibbs free energy of activation (at 298.15 K) for steps 1b to 1e were listed in Table S2. The OOH_{ad} formation step (1b) was found has the highest free energy of activation of 0.36 eV. The transition state for this step was displayed in Fig. 5a. On one type of Co-doped PdO(101) surface (see Fig. 5b), a new mechanism for the ORR with lower barrier was found. This new mechanism involves following six elementary steps:



We also listed the transition state structure and Gibbs free energy of activation for steps 2b to 2e in Table S3. The last step 2f is similar to the step 1e on the pure PdO surface. On the Co-doped surface, the OH^* transferring step from Co to Pd atom is found as the rate-determining step (2e), which has the highest Gibbs free energy of activation of 0.19 eV. The energy profile for this step were presented in Fig. 5b. The energy barrier of the rate-determining on Co-doped PdO surface is obviously lower than that on pure PdO surface. On the Co-doped Pd (101) surface, there is nearly no barrier for the OOH_{ad} formation step (2b). The free energy of activation for the O–O bond breaking step on Co-doped surface (2c, 0.12 eV) is also substantially lower than that on pure PdO (101) surface (step 1c, 0.33 eV). The stronger interaction

between OH, H_2O and Co is very important to reduce the energy barrier of ORR. The synergy between Pd and Co clearly facilitates the ORR.

The enhanced electrocatalytic activities mainly be attributed to the following factors: (i) The structure of PdCo-300, in which the PdO and Co_3O_4 present in PdO- Co_3O_4 mixed phase boosts the electrocatalytic activity. Specifically, the PdO domain was surrounded by the Co_3O_4 domain, which produced closely mutually connected interfaces. At the interface, the exchange of Co and Pd species can result in a valence states transformation of Pd and Co ($\text{Pd}^{2+} + \text{Co}^{3+} \rightarrow \text{Pd}^{\delta+} + \text{Co}^{2+}$). The existence of high valence state $\text{Pd}^{\delta+}$ with a downshift of the d-band center could decrease the superficial coverage by the generated OH, leading to the release of more active sites for O_2 adsorption, and thus improving the ORR activity. Meanwhile, Co^{3+} partially reduced to Co^{2+} in the Co_3O_4 , producing a large number of oxygen vacancies. these oxygen vacancies may improve the electronic conductivity, facilitate the OH^- adsorption, provide more electrochemically active sites, and thus enhance the electrocatalytic activity for OER. (ii) The synergistic effect between the Co and Pd ions in the interface, which have different adsorption energy to intermediate species, and change the reaction to a path with small barrier.

4. Conclusions

In summary, we have successfully synthesized the PdO-doped Co_3O_4 nanoparticles with closely mutually connected interfaces. The PdCo-300 exhibits an excellent electrocatalytic performance for ORR in alkaline electrolyte with the current density of -5.07 mA cm^{-2} and the half-wave potential of 0.83 V, which is very close to those of commercial Pt/C (-5.1 mA cm^{-2} , 0.85 V), a higher electrocatalytic activity for the OER with a potential of 1.58 V at a current density of 10 mA cm^{-2} , 60 mV negative than that of commercial RuO_2 (1.64 V). Meanwhile, the PdCo-300 nanoparticles also exhibit excellent durability during long-term cycling in the alkaline environment due to excellent stability of the special heterostructure. Moreover, the PdCo-300 nanoparticles are prepared by a facile procedure, which can be easily extended to the preparation of other multifunctional material for a broad range of applications such as solar cells, fuel cells and other heterogeneous catalysis.

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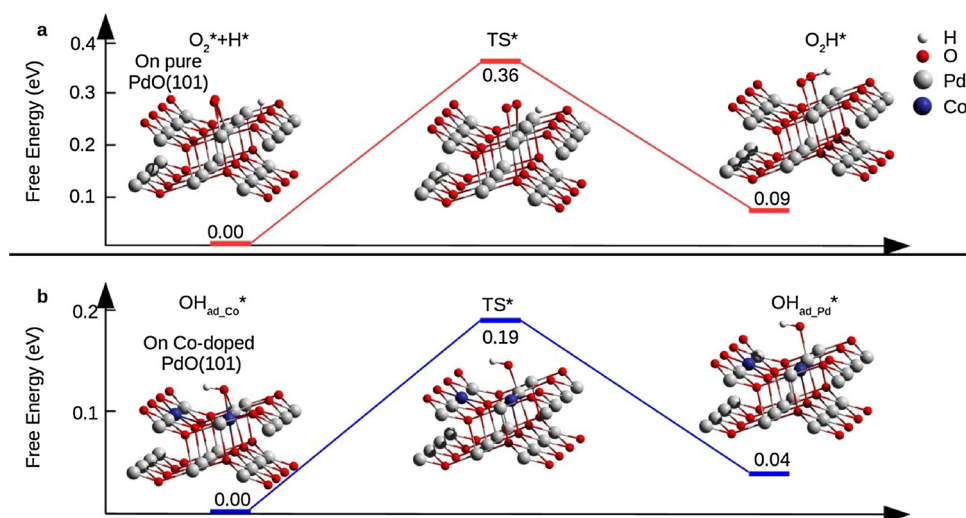


Fig. 5. The free energy profile for some key steps of ORR on pure and Co-doped PdO (101) surface. (a) The OOH^* formation step on PdO (101); (b) The OOH^* formation step on Co-doped PdO (101).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.10.040>.

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